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Thermochemistry of hydrogen bonding of linear and cyclic amides in proton acceptors media

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ABSTRACT

In present work thermochemistry of hydrogen bond formation of linear (acetamide (AA), *N*-methylacetamide (NMA), *N,N*-dimethylacetamide (DMAA)) and cyclic amides (2-pyrrolidone (Py), *N*-methyl-2-pyrrolidone (MPY)) in the medium of proton acceptors (B) was studied. Enthalpies of solution of amides in nitriles, ketones, esters, ethers and amines were measured at 298.15 and infinite dilution conditions. Enthalpies of hydrogen bonding of studied solutes with proton acceptor solvents were determined on the basis of experimental data. It was shown that proton donor properties of 2-pyrrolidone are more pronounced than linear amides. Enthalpies of hydrogen bonding of acetamide in proton acceptors are twice more than *N*-methylacetamide due to formation of 1:2 complexes.

1. Introduction

Amides are organic compounds which contain of N—H and C=O groups and capable to form hydrogen bonds with proton donor and proton acceptor organic molecules. These hydrogen bonds are similar to those formed in proteins and peptides molecules [1,2]. Hydrogen bonds play crucial role in conformational stability of biomolecules. The study of them in proteins and peptides by experimental methods is very difficult task, therefore approach based on studies of model compounds can be used in this case. Amides are the closest model compounds to study the hydrogen bonds in proteins and peptides [3–6]. Moreover, linear and cyclic amides themselves have wide practical applications as solvents for the separation different mixtures [7], as electrolytes [8–10], used as ligands in catalysis [11], and also amides are involved as components of anticancer drugs [12,13]. It should be noted that physical-chemical properties of amides in all above-mentioned systems are realized through different types of intermolecular interactions. Hydrogen bonds are the most important among them.

The formation of hydrogen bonds of amides with organic molecules was studied by different experimental methods: IR-spectroscopy [3,4,14], UV-spectroscopy [4,5], NMR-spectroscopy [15,16], solution calorimetry [17–20] and computational chemistry [4,5,21–23]. Authors of these works have analyzed strengths of hydrogen bonds of amides with proton acceptors [4,5,15,18,24], proton donors [24], aliphatic alcohols and water [4,5,18,24]. Also, self-association of amides through N—H···O=C hydrogen bonds was studied [25–27]. At the same time such phenomena as cooperativity of hydrogen bonds occurs in amide solutions [25–28], which changes the acid-base properties of the molecules.

In works [15,16] it was shown that increase of alkyl substituents in the molecules of acetamides significantly to decrease the enthalpy of association. It was noted that enthalpies of association of amides in tetrachloromethane are higher than in dioxane due to breaking of amide–amide hydrogen bonds [15]. Spencer et al. [18] have shown that strength of one hydrogen bond of acetamide in proton acceptors is weaker than enthalpy of hydrogen bond in *N*-methylacetamide complexes, respectively. Kimura et al. [19] have shown that aprotic amides of linear and cyclic structure (*N,N*-dimethylpropanamide and *N*-methyl-2-pyrrolidone) to have equal proton acceptor ability. Morgan and Kopp [20] have investigated thermochemistry of solvation of protic amides (2-pyrrolidone and *N*-methylpropionamide) in proton acceptor and proton donor solvents. Enthalpies of solvation of linear and cyclic NH-amides in proton donor solvents are close to each other, unlike enthalpies of solvation of amides in proton acceptors solvents. Apparently, the differences between the enthalpies of solvation of linear and cyclic amides are related to the different strength of intermolecular interactions of amides in proton acceptor solvents. In order to assess the influence of a cyclic structure on proton donor properties of

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